Hydrogen Desorption from $LaNi_5$ Hydrides Stabilized with SO_2 and CO

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The stabilization of the $LaNi_5H_6$ hydride was performed by poisoning the surface with CO or SO_2, in gaseous or liquid phase. The enhancement of the retention time of hydrogen in the hydride was confirmed for the SO_2 treatment, if employed in a liquid phase, compared to the performance of the CO surface treatment. The dehydrogenation kinetics of the untreated, CO-treated, and liquid SO_2-treated samples were investigated at 373 K, by the closed-system technique. We found that the dehydrogenation was complete within 120 s for the untreated sample, whereas it took more than 21.6 ks for the liquid SO_2 treated $LaNi_5$. The hydrogenation of organic compound (1-octene) using treated $LaNi_5$ hydrides as catalysts was investigated in order to study whether the hydrogen was available or not after the treatments with poison. The hydrogenation of 1-octene was not successfully carried out with the liquid SO_2-stabilized hydride, whereas it proceeded well with the gaseous SO_2-treated hydride and the gaseous CO-treated one. This behavior is due to the difference in mechanism of hydrogen confinement. The determination of sulfur and carbon amounts in the treated and untreated samples and the XPS and FTIR analysis provided useful information for the understanding of this mechanism.

Introduction

$LaNi_5$ hydrides are actively studied as materials for battery electrodes, because of their hydrogen-storage properties and for their good catalytic activities for the hydrogenation of organic compounds. The use of rare-earth intermetallic compounds as catalysts for the production of hydrocarbons from carbon monoxide and hydrogen gas was investigated by Takeshita, Wallace, and co-workers.[1] $LaNi_5$ hydrides were used by Imamura and co-workers and then by other authors for the hydrogenation of organic compounds.[2−4] This technique permitted use of hydrogen as molecules desorbed from the hydrides rather than from a surrounding gas. Since the $LaNi_5H_{6.5}$ hydride exhibits an equilibrium plateau pressure of 0.2 MPa,[5] one cannot handle the hydride in air. The impurities found in the hydrogen gas, such as carbon monoxide and other sulfur compounds,[6] have the effect of poisoning the hydride surface. Therefore, Gualtieri et al. have used SO_2 to confine hydrogen in the hydride.[7] Recently, the stabilization of $LaNi_5H_x$ surfaces with SO_2 was analyzed in more detail,[8] showing the reaction of sulfur at the surface sites to form sulfates and sulfides on the $LaNi_5$ hydride surface.

As reported in a previous paper,[9] the hydrogen confinement was performed with a poisoning gaseous CO treatment. It has been found that one chemisorbed CO molecule can confine 10^4 H_2 molecules. This CO treated hydride has served as a catalyst for hydrogenation reactions of 1-octene and acetophenone,[10] and it was confirmed that hydrogen confined in the hydride can be available for the hydrogenation reactions.

We also reported that the use of a liquid-phase SO_2 treatment instead of a gaseous one extends the retention time of hydrogen in the $LaNi_5$ hydride,[11] whereas no difference between the liquid and the gaseous phase was found for the CO-treated hydrides. This was understood on the basis of the dissociative bahavior of the SO_2 molecules in chemisorption, whereas CO molecules chemisorb associatively. We also demonstrated that a slight decrease in the temperature of the gaseous CO-treated hydride stabilization yields improvements in the efficiency of the confinement of hydrogen. Finally, the hydrogen retention time was found to be considerably longer for the liquid SO_2 treatment than for the CO one.

In the present study, to confirm whether the hydrogen in the treated hydrides can be available or not, we carried out the dehydrogenation of the untreated and treated samples at 373 K by the closed-system technique, and the hydrogenation of an organic compound

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(1) Coon, V. T.; Takeshita, T.; Wallace, W. E.; Craig, R. S. *J. Phys. Chem.* **1976**, *80*, 1878.

(2) Soga, K.; Imamura, H.; Ikeda, S. S. *Chem. Lett.* **1976**, 1299.

(3) Imamoto, T.; Mita, T.; Yokoyama, M. *J. Org. Chem.* **1987**, *52*, 5695.

(4) Johnson, J. R.; Gavra, Z.; Reilly, J. J. *Z. Phys. Chem.* **1993**, *181*, 391.

(5) Buschow, K. H. J.; Bouten, P. C. P.; Miedema, A. R. *Rep. Prog. Phys.* **1982**, *45*, 937.

(6) Sandrock, G. D.; Goodell, P. D. *J. Less-Common Met.* **1984**, *104*, 159.

(7) Gualtieri, D. M.; Narasimhan, K. S. V. L.; Takeshita, T. *J. Appl. Phys.* **1976**, *47*, 3432.

(8) Myhra, S.; Kisi, E. H.; Gray, E. M. *J. Alloys Comp.* **1995**, *224*, 305.

(9) Sakaguchi, H.; Tsujimoto, T.; Adachi, G. *J. Alloys Comp.* **1995**, *223*, 122.

(10) Sakaguchi, H.; Gotoh, Y.; Adachi, G. *Chem. Lett.* **1996**, *10*, 905.

(11) Corré, S.; Gotoh, Y.; Sakaguchi, H.; Fruchart, D.; Adachi, G. *J. Alloys Comp.*, in press.

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(1-octene) using liquid or gaseous SO_2-treated $LaNi_5$ hydrides as catalysts. These results were compared with those of the previous studies of CO-treated $LaNi_5$ hydrides.[9,10] Sulfur and carbon contents in the treated and untreated hydrides were determined. The surface conditions of the samples were analyzed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy.

Experimental Section

Samples Preparation. $LaNi_5$ ingots were supplied by Santoku Metal Industry Co., Ltd., Kobe, Japan. The synthesis method was arc melting. The samples were crushed into powder under an argon atmosphere, and 1.3 g (3 mmol) of the powder was introduced into a stainless steel vessel. The activation was carried out under 1 MPa of hydrogen gas, cycling temperature from 273 to 373 K.

Then, the hydrogen gas was quickly removed (in less than 120 s), and all poisoning treatments were performed during 300 s, according to a method previously described.[9,11] The liquid SO_2 treatment was realized at 273 K, the gaseous SO_2 one at room temperature with a pressure of 0.2 MPa, and the gaseous CO one also at room temperature, at pressures of 0.2 or 0.9 MPa. The poisoning gas was removed from the sample holder in less than 120 s. The resulting treated sample was then surrounded by 0.1 MPa of helium during 1.8 ks, for thermal equilibration. The purity of gases was 99.9995% for the hydrogen gas and 99.9% for the carbon monoxide or the sulfur dioxide.

Some precautions must be taken when using carbon monoxide and sulfur dioxide, since these species are very dangerous: we connected the experimental setup to two bottles. One was refilled with a mixture of copper sulfate and ammoniacal water to trap the carbon monoxide when evacuating the setup from the poisoning gas. The other one was refilled with aqueous sodium hydroxide to trap the sulfur dioxide. After each experiment, the setup was heated at 473 K and the remaining gas was pumped during several hours.

The poisoning surface treatments to the activated $LaNi_5$ hydrides led to the preparation of three different types of samples: liquid SO_2-treated, gaseous SO_2-treated, and gaseous CO-treated $LaNi_5$ hydrides.

The powders were analyzed by X-ray diffraction (Cu Kα radiation) with a MAC Science M18XHF-SRA diffractometer to determine the amount of remaining hydrogen versus time, calculated according to a method previously reported.[9]

The sulfur and carbon contents in the powders were determined with a Horiba EMIA-810 type apparatus for the raw material, the activated powder, and the treated hydrides.

X-ray photoelectron spectroscopy was undertaken with a 5500MT-type ULVAC-PHI spectrometer (Mg wavelength, 1253.6 eV) and Fourier transform infrared spectroscopy with a FTIR-8000 Shimadzu apparatus, in order to identify the chemical species present in the untreated and in the SO_2-treated $LaNi_5$ powders.

Dehydrogenation Kinetics Measurements. The dehydrogenation kinetics measurements of the untreated, the 0.9 MPa gaseous CO-treated, and the liquid SO_2-treated samples were performed at 373 K in a closed-system volume (2.3×10^{-1} m^3). After the preparation of the treated and untreated samples, the gas (CO or SO_2 in the case of treated sample, H_2 in the case of untreated sample) remaining in the sample holder was evacuated at 273 K for 180 s. This relatively low temperature permitted maintenance of the β-phase present (around six hydrogen atoms/$LaNi_5$ formula) during the evacuation. The sample holder was then closed, and a temperature of 373 K was immediately applied to the sample to provoke the dehydrogenation. The pressure in the closed system was recorded in function of time.

Hydrogenation of Organic Compounds. 1-Octene was obtained from Wako Pure Chemical Ind., with a purity of 95%. It was distilled before use. 1-Octene (1 mL) was dissolved in cyclohexane (a total volume of 5 mL). This solution was then introduced into a vessel containing the treated hydride powder. The reaction took place at a given temperature, during 14.4 ks, and was performed with a 2000 rpm stirrer.

After reaction, gas chromatography was performed with a Shimadzu GC-8A apparatus (detector FID, N_2 as carrier gas) equipped with a column of 5% PEG 20M on Shimalite NAW (68/80 mesh) to determine the yield of *n*-octane present in the solution.

The amount of remaining hydrogen in the hydrides was then calculated from XRD patterns.

The sulfur and carbon contents in the powders were also analyzed as described above, in order to determine the amount of carbon and sulfur which could have been dissolved in the solution during the reaction.

Scanning electron microscopy permitted to check the surface smoothness, which could be modified by the deposition of sulfur.

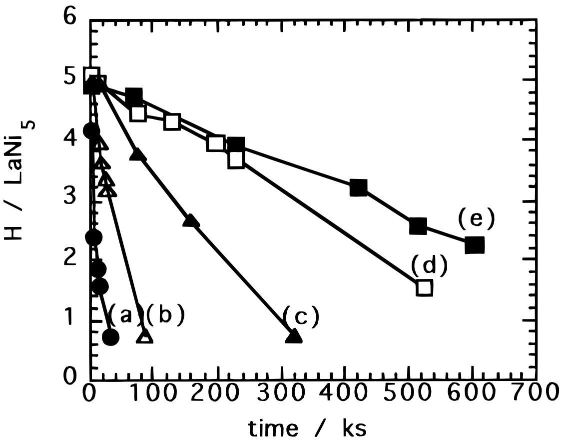

Figure 1. Effect of the poisonous species on the $LaNi_5$–hydride stabilization at 298 K in air: (a) no treatment, (b) 0.2 MPa gaseous SO_2 treatment, (c) 0.2 MPa gaseous CO treatment, (d) 0.9 MPa gaseous CO treatment, and (e) liquid SO_2 treatment.

Results and Discussion

Figure 1 shows the performance of the hydride after treatment with the poison (gaseous SO_2, liquid SO_2, and gaseous CO at 0.2 and 0.9 MPa) on the retention of hydrogen in the $LaNi_5$ hydride at 298 K in air together with the result for the untreated hydride. The hydrogen retention time was slightly increased by the gaseous SO_2 surface treatment. The gaseous CO treatments performed at 0.2 or 0.9 MPa provided a better hydrogen retention time, and the latter treatment permitted maintenance of four hydrogen atoms/$LaNi_5$ formula after 220 ks. The most effective treatment to the hydrogen confinement was the liquid SO_2 treatment, leading to the time of 240 ks for four hydrogen atoms/$LaNi_5$ formula. These results are in good agreement with our previous work.[9,11] Therefore, in comparing the gaseous CO treatment and the gaseous SO_2 one, both performed at 0.2 MPa, the CO treatment appeared to be the most suitable for the retention of hydrogen. To the contrary, the liquid SO_2 treatment had a better efficiency than that of the liquid CO one. The difference in hydrogen retention between the 0.2 MPa CO-treated sample (curve c) and the 0.9 MPa CO one (curve d) could be explained by the fact that at higher pressure, the CO molecules can better cover the surface within the 300 s of the treatment. The time dependence of the CO gaseous treatment to obtain different hydrogen retention times is currently studied.

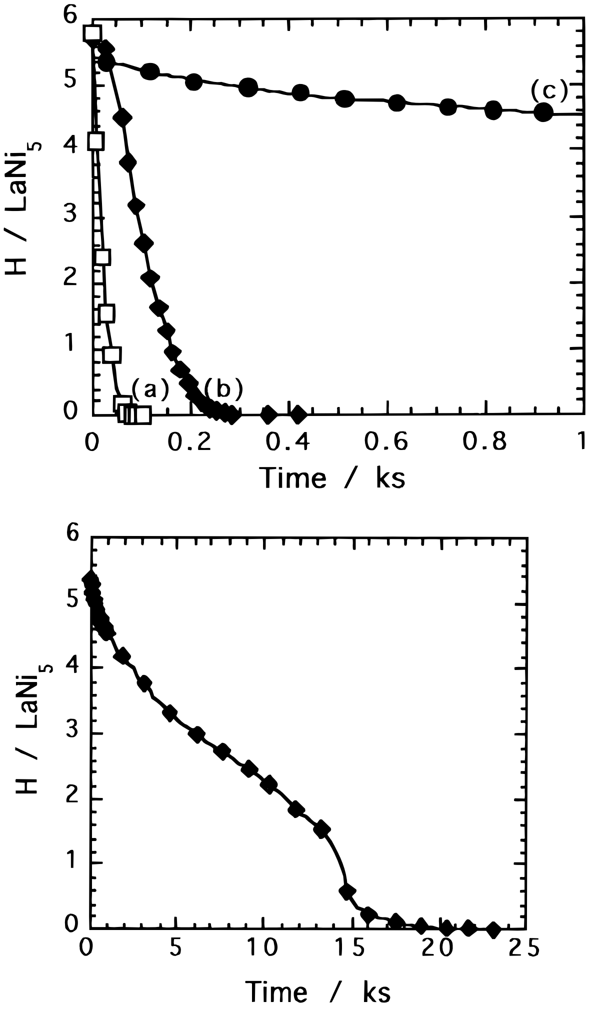

Figure 2. (a, top) Dehydrogenation kinetic at 373 K in vacuo for the $LaNi_5$ samples with (a) no treatment, (b) 0.9 MPa gaseous CO treatment, and (c) liquid SO_2 treatment. (b, bottom) Dehydrogenation kinetics at 373 K in vacuo for the liquid SO_2-treated $LaNi_5$ sample (full scale).

Figure 2a shows the change in hydrogen concentration during dehydrogenation versus time for the untreated, gaseous CO-treated, and liquid SO_2-treated samples. We observed a complete dehydrogenation for the untreated sample within 90 s, whereas the CO-treated sample exhibited slower dehydrogenation kinetics with complete dehydrogenation in 300 s. Dramatically slow dehydrogenation kinetics were observed for the liquid SO_2-treated sample. After 5.4 ks at 373 K, more than three hydrogen atoms/$LaNi_5$ formula still remained in the powder. The dehydrogenation was finished after 23.4 ks, as shown in Figure 2b. A temperature of 373 K does not permit the desorption of the CO molecules, which dominantly appears at 420 K.[12] These kinetics are in good agreement with those given at 298 K in Figure 1. The liquid SO_2 treatment shows here its great application potentiality as a treatment permitting the observation of powders with high hydrogen content (β-phase), even at high temperature and in vacuo.

To confirm whether the hydrogen in the SO_2-treated hydrides can be available or not, we carried out the hydrogenation of 1-octene using the liquid SO_2 and the gaseous SO_2-treated $LaNi_5$ hydrides as catalysts. The hydrogenation of 1-octene gives only one product, which is *n*-octane. The performance is summarized in Table 1 and is compared to that of the 0.9 MPa gaseous CO-treated $LaNi_5$ hydride[10] and to that of the untreated $LaNi_5$ hydride. The presence of *n*-octane has not been detected for the liquid SO_2-treated catalyst, whereas a yield of 95% of *n*-octane was obtained for the reaction using the CO-treated hydride at 313 K. The gaseous SO_2-treated hydride exhibited similar performance, i.e., a yield of 92% of *n*-octane at 313 K. It should be noted that the hydrogen concentration in $LaNi_5H_x$ after reaction remained always greater than 1.7 ± 0.2. This behavior is directly related with the efficiency of the surface treatment. The better the surface-treatment efficiency, the worse the catalytic activity of the treated $LaNi_5$ hydrides for the hydrogenation reaction.

Table 2 shows the sulfur and carbon contents in the raw $LaNi_5$, the activated sample and the hydride samples treated with liquid SO_2, 0.2 MPa of SO_2 gas, or 0.9 MPa of CO gas. Traces of sulfur were found in the two untreated samples (the raw material and the activated sample). The liquid SO_2-treated $LaNi_5$ powder, however, contained 218 ± 10 ppm of sulfur. As expected, the gaseous SO_2-treated sample contained a lower amount of sulfur (163 ± 10 ppm). The sulfur deposition is more efficient for the liquid SO_2 treatment since the entropy term is favorable to solid/liquid system in comparison with the solid/gas one. The gaseous CO treated sample retained 370 ± 10 ppm of carbon.

To understand whether the sulfur or carbon amount was changed or not during the hydrogenation reaction, a comparison was made between the amounts found before and after the hydrogenation reaction of 1-octene, for the liquid SO_2-treated sample and the 0.9 MPa gaseous CO-treated one. The results are summarized in Table 3. The carbon content in the gaseous CO-treated $LaNi_5$ changed from 370 ± 10 ppm before the hydrogenation reaction of 1-octene to 416 ± 10 ppm after the reaction. The slight increase of carbon was certainly due to the contamination by the organic compound itself (1-octene has eight carbon atoms). It is believed that the CO molecules stay at the surface during the reaction or are replaced by carbon atoms from the decomposition of 1-octene, if any. The liquid SO_2-treated hydride had 218 ± 10 ppm of sulfur before the hydrogenation reaction, and 235 ± 10 ppm afterward. Considering the error bars, we can say that the sulfur amount in the hydrides has not changed during the reaction of 1-octene. Scanning electron microscopy was also performed on liquid SO_2-treated hydrides obtained before and after the hydrogenation of 1-octene. Before the hydrogenation reaction, the sample exhibited some "islands" of sulfur precipitated on its surface.[11] After the hydrogenation, these islands did not exist any more, indicating the dissolution of a large amount of sulfur in the solution (1-octene/cyclohexane). Since the sulfur amount has not changed, it appears that these islands first dissolved in the organic solution and were precipitated uniformly on the hydride surface when the solution was removed after the reaction, as the powder was not rinsed before the sulfur analysis.

From XPS analysis, nickel, sulfate $NiSO_4$, and sulfide NiS were found at the powder surface layer, down to a depth of 22 nm, in good agreement with the litera-

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(12) Yates, Jr., J. T.; Goodman, D. W. *J. Phys. Chem.* **1980**, *73*, 5371.

Table 1. Hydrogenation of 1-Octene with Liquid SO_2, 0.2 MPa Gaseous SO_2, 0.9 MPa CO Treated and Untreated $LaNi_5$ Hydrides

		temp (K)				
		273	313	333	343	ref
liquid SO_2-treated hydride	yield of *n*-octane (%)[a]	*c*	*c*	*c*	*c*	this work
	$H/LaNi_5$[b]	6.2 ± 0.2	5.3 ± 0.2	5.5 ± 0.2	5.5 ± 0.2	this work
0.2 MPa gaseous SO_2-treated hydride	yield of *n*-octane (%)[a]	*c*	92 ± 2			this work
	$H/LaNi_5$[b]	5.6 ± 0.2	1.7 ± 0.2			this work
0.9 MPa gaseous CO-treated hydride	yield of *n*-octane (%)[a]	6 ± 2	95 ± 2			8
	$H/LaNi_5$[b]	6.4 ± 0.2	3.4 ± 0.2			8
untreated hydride	yield of *n*-octane (%)[a]	99 ± 2				this work
	$H/LaNi_5$[b]	5.8 ± 0.2				this work

[a] Determined by GC analysis. [b] Hydrogen concentration in $LaNi_5H_x$ after reaction (before reaction, $x = 6.5 \pm 0.2$). [c] Not detected.

Table 2. Sulfur and Carbon Contents in the Treated and Untreated $LaNi_5$ Powders

	sulfur content (ppm)[a]	carbon content (ppm)[a]
raw material	9 ± 3	231 ± 10
activated sample	29 ± 4	368 ± 10
0.9 MPa gaseous CO-treated sample	3 ± 1	370 ± 10
liquid SO_2-treated sample	218 ± 10	375 ± 10
0.2 MPa gaseous SO_2-treated sample	163 ± 10	488 ± 10

[a] Determined with a HORIBA sulfur/carbon analyzer.

Table 3. Sulfur and Carbon Amounts in the Liquid SO_2-Treated $LaNi_5$ and in the 0.9 MPa Gaseous CO-Treated $LaNi_5$ Powders, before and after Hydrogenation Reaction of 1-Octene

	sulfur content (ppm)[a] before hydrogenation reaction of 1-octene	sulfur content (ppm)[a] after hydrogenation reaction of 1-octene	carbon content (ppm)[a] before hydrogenation reaction of 1-octene	carbon content (ppm)[a] after hydrogenation reaction of 1-octene
0.9 MPa gaseous CO-treated sample	3 ± 1	6 ± 3	370 ± 10	416 ± 10
liquid SO_2-treated sample	218 ± 10	235 ± 10	471 ± 3	447 ± 10

[a] Determined with a HORIBA sulfur/carbon analyzer.

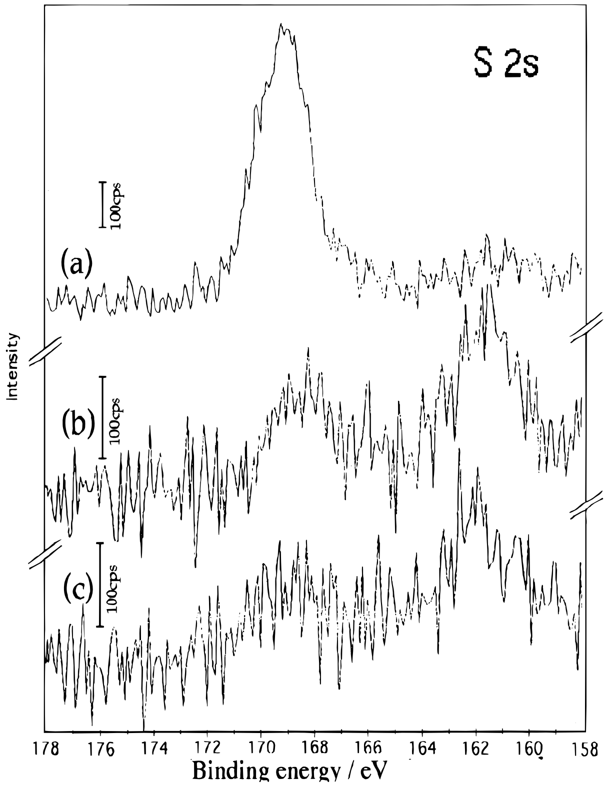

Figure 3. Intensity of the sulfur peak "2s" from XPS analysis for the liquid SO_2-treated $LaNi_5$ sample: (a) as prepared, (b) after etching, 7.5 Å, and (c) after etching, 22.5 Å.

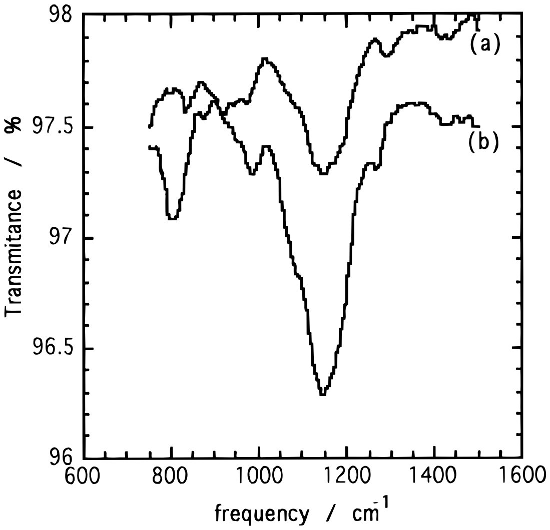

Figure 4. Fourier transform infrared spectra for (a) the 0.2 MPa gaseous SO_2-treated $LaNi_5$ and (b) the liquid SO_2 one.

ture.[7,11] Figure 3 represents the intensity of the sulfur 2s peak for the liquid SO_2 sample as prepared, after etching 7.5 Å and after etching 22.5 Å. The observation of sulfur down to the surface (after etching) permitted to check the penetration of sulfur in the alloy particle, leading to the understanding of the excellent efficiency of the liquid SO_2 treatment. The FTIR patterns for the liquid SO_2- and the gaseous SO_2-treated samples are shown in Figure 4. The band positions at 985 and at 1139 cm^{-1} were attributed to the sulfate ion, confirming the XPS results above. This is consistent with the work of Blyholder and co-workers.[13] The $LaNi_5$ surface is considered to be composed of nickel and of La_2O_3 (or $La_2(OH)_3$).[14] The nickel atoms are the active sites for the dissociation (and recombination) of H_2 molecules

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(13) Blyholder, D.; Cagle, G. W. *Environ. Sci. Technol.* **1971**, *5*−*2*, 158.

(14) Schlapbach, L. *J. Phys. F: Met. Phys.* **1980**, *10*, 2477.

from the surrounding gas into hydrogen atoms.[15] Hydrogen atoms diffuse then into the bulk and transform progressively $LaNi_5$ into $LaNi_5H_6$. Several layers of nickel were affected by the change of chemical form into sulfides and sulfates. The lanthanum oxides were also certainly covered by sulfur. It is then difficult for the hydrogen atoms to find a free active nickel site and to recombine into a H_2 molecule. The desorption of the liquid SO_2 treated $LaNi_5$ hydride had then very slow kinetics. These results suggest a clear difference in the mechanism of hydrogen confinement between the SO_2 and CO surface treatments. Carbon monoxide reversively adsorbs on the hydride surface in the molecular form and bonds to Ni atoms.[9] Therefore, CO exists only at the top surface, the deeper nickel atoms are not affected by the carbon monoxide molecules and hydrogen is easily available. Sulfur dioxide molecules, however, chemisorb dissociatively, and the resulting sulfur diffuses into the bulk to form sulfur compounds. The thick layer of sulfates and sulfides appears to be more effective to confine hydrogen. To the contrary, if we consider using the hydrogen from the sealed hydride, the liquid SO_2 treatment would be placed at a disadvantage because it is difficult to take out hydrogen from the hydride.

Conclusion

It was confirmed that the liquid SO_2 surface treatment was very efficient for the stabilization of the $LaNi_5$ hydrides. At 298 K in air, four hydrogen atoms per $LaNi_5$ formula remained after 340 ks. At 373 K in vacuo, the dehydrogenation kinetics were still very slow and four hydrogen atoms per $LaNi_5$ formula remained after 2.4 ks. This liquid SO_2 treatment had a better efficiency than the CO treatment from our previous work.

Although this treatment is highly efficient, it is not possible to use the sealed hydrogen in other reactions. On the other hand, the hydrogenation of organic compounds proceeded well with the gaseous CO-treated $LaNi_5$ hydride used as a catalyst or the gaseous SO_2-treated $LaNi_5H_x$.

This behavior was understood from the difference in chemisorption mechanism between CO and SO_2 molecules. The SO_2 molecules form a thick sulfur layer on the hydride surface (as sulfur, sulfates, and sulfides), whereas the CO molecules chemisorb associatively and do not completely avoid the recombination process of hydrogen atoms into H_2 molecules.

Therefore, the liquid SO_2 surface treatment is very promising as a technique permitting the study of hydrides in various conditions (high temperature, air, vacuum, etc.), whereas the use of the gaseous SO_2-treated $LaNi_5$ hydride as catalyst for the hydrogenation of 1-octene was successfully demonstrated, showing the possibility to release the confined hydrogen.

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(15) Wallace, W. E.; Karlicek, Jr., R. F.; Imamura, H. *J. Phys. Chem.* **1979**, *83*, 1708.